

This Page Is Inserted by IFW Operations  
and is not a part of the Official Record

## **BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning documents *will not* correct images,  
please do not report the images to the  
Image Problem Mailbox.**

**THIS PAGE BLANK (USPTO)**

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
1 March 2001 (01.03.2001)

PCT

(10) International Publication Number  
**WO 01/14496 A1**

(51) International Patent Classification<sup>7</sup>: C09K 3/14,  
H01L 21/302, C09G 1/02

(21) International Application Number: PCT/US00/23052

(22) International Filing Date: 23 August 2000 (23.08.2000)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
60/150,443 24 August 1999 (24.08.1999) US  
60/224,686 11 August 2000 (11.08.2000) US

(71) Applicant: RODEL HOLDINGS, INC. [US/US]; Suite  
1300, 1105 North Market Street, Wilmington, DE 19899  
(US).

(72) Inventors: COSTAS, Wesley, D.; 115 Milano Drive,  
Bear, DE 19701 (US). SHEN, James; 9 Yosemite Drive,  
Bear, DE 19701 (US). MANDIGO, Glenn, C.; 3576 Gar-  
net Mine Road, Boothwyn, PA 19061 (US). THOMAS,

Terence, M.; 209 Cullen Way, Newark, DE 19711 (US).  
LACK, Craig, D.; 438 Greenwood Drive, Wilmington,  
DE 19808 (US). BARKER, Ross, E., II; 114 Anglin  
Drive, Newark, DE 19713 (US).

(74) Agent: BENSON, Kenneth, A.; Rodell Holdings, Inc.,  
1105 North Market Street, Suite 1300, Wilmington, DE  
19899 (US).

(81) Designated States (*national*): JP, KR, SG.

(84) Designated States (*regional*): European patent (AT, BE,  
CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC,  
NL, PT, SE).

**Published:**

- With international search report.
- With amended claims.

*For two-letter codes and other abbreviations, refer to the "Guid-  
ance Notes on Codes and Abbreviations" appearing at the begin-  
ning of each regular issue of the PCT Gazette.*

(54) Title: COMPOSITIONS FOR INSULATOR AND METAL CMP AND METHODS RELATING THERETO

(57) Abstract: A composition is provided which is useful for the polishing of a semiconductor wafer substrate comprising an organic polymer having a backbone comprised of at least 16 carbon atoms, the polymer having a plurality of moieties with affinity to surface groups on the semiconductor wafer surface. Another composition is provided which is useful for the polishing of a semiconductor wafer substrate comprising a surfactant having a carbon chain backbone comprised of at least 16 carbon atoms.

WO 01/14496 A1

5       **COMPOSITIONS FOR INSULATOR AND METAL CMP AND METHODS**  
          **RELATING THERETO**

          This application claims the benefit of U.S. Provisional Application Serial  
10       Number 60/150,443 filed August 24, 1999 and U.S. Provisional Application filed  
          8/11/00.

**BACKGROUND OF THE INVENTION**

15       **Field of the invention**

          The present invention relates to the polishing and planarization of integrated  
circuit surfaces, particularly those comprising silicon dioxide films (TEOS, thermal  
oxide or BPSG), low-K ILD films, silicon nitride films, metal films (lines) and the  
mixtures of these.

20

**Discussion of Related Art**

          CMP is an enabling technology used in the semiconductor industry to  
remove/planarize various thin films from the surface of semiconductor substrates  
during the production of IC. Various types of abrasives have been used for CMP.

25       The polishing pad, typically made of polymer materials, is another important part in  
the CMP process. Particles of silicon dioxide, metal oxide (alumina, ceria, titania  
and zirconia etc.) or a mixture of the like are typically used as the abrasive in CMP  
slurries.

30       Achieving IC wafer planarization with smooth, scratch-free and low defect  
surfaces is greatly challenged by the presence of abrasive particles and the micro-  
asperities of the polymer pads. A CMP slurry which is not properly formulated will  
generate scratches and residues on the polished surfaces. The scratches may result  
from the trace tracks of the particles (slurry abrasives and residue from removed  
35       materials), while the residue coating may come from the gelled slurries and the re-  
deposition of the removed materials (metal oxide in the case of metal CMP and  
silanol or silicates in the case of silicon oxide CMP.) The dense scratching texture  
will heavily contribute to the higher level of roughness on the wafer surfaces. It has

been observed that the slurry coating and re-deposition of residue will preferentially occur in the dense pattern areas, especially small features and interconnection lines in areas where the surface energy is high and the residue can be readily accommodated.

5        USP 5,704,987 addresses the problem of removing residual slurry particles adhered to a wafer surface after chemical-mechanical polishing. Proposed is a two step cleaning operation. The first step uses a basic aqueous solution of a nonionic polymeric surfactant; the second step uses purified water.

10        USP 5,783,489 discusses the use of surfactants, stabilizers, or dispersing agents to promote stabilization of a polishing slurry including oxidizing agents against settling, flocculation and decomposition. Surfactants may be anionic, cationic, nonionic, or amphoteric. It was found that the addition of a surfactant may be useful to improve the within-wafer-non-uniformity (WTWNU) of the wafers, thereby  
15        improving the surface of the wafer and reducing wafer defects.

      The present invention provides compounds that can be used in CMP slurries to prevent scratching, minimize surface roughness, and eliminate coating of gelled slurries or residue on the IC wafer surfaces. The chemical compounds listed in this  
20        patent work effectively with abrasive particles including, but not limited to, silicon dioxide, metal oxides and any other inorganic oxides, and mixtures of the like. The slurries of this invention work effectively on CMP processes for sheet wafers, pattern wafers with the films/lines of silicon dioxide (TEOS, BPSG, thermal oxide), low K polymers, silicon nitride and metals, as well as mixtures of the like.

25

## SUMMARY OF THE INVENTION

      A composition is provided which is useful for the polishing of a semiconductor wafer substrate comprising an organic polymer having a backbone  
30        comprised of at least 16 carbon atoms, the polymer having a plurality of moieties with affinity to surface groups on the semiconductor wafer surface.

Another composition is provided which is useful for the polishing of a semiconductor wafer substrate comprising a surfactant having a carbon chain backbone comprised of at least 16 carbon atoms.

5

Yet another polishing composition is provided for the chemical mechanical polishing of semiconductor wafers having a metal circuit comprises an aqueous composition having a pH of under 5.0 and comprises polyacrylic acid having a number average molecular weight of about 20,000 – 150,000, or blends of high and low number average molecular weight polyacrylic acids.

10

A further aspect of this invention is the method of polishing a semiconductor wafer substrate, wherein the substrate is pressed against a polishing pad, the substrate and the pad are moved relative to each other, and a polishing composition is applied to the pad during the polishing operation, the polishing composition comprising an organic polymer having a backbone comprised of at least 16 carbon atoms, the polymer having a plurality of moieties with affinity to surface groups on the semiconductor wafer surface.

15

Yet another aspect of this invention is the method of polishing a semiconductor wafer substrate, wherein the substrate is pressed against a polishing pad, the substrate and the pad are moved relative to each other, and a polishing composition is applied to the pad during the polishing operation, the polishing composition comprising a surfactant having a carbon chain backbone comprised of at least 16 carbon atoms.

20

25

The compositions of this invention may optionally further comprise one or more of the following: submicron abrasive particles, a dispersing agent, an oxidizing agent, and a complexing agent.

30

## DESCRIPTION OF THE PREFERRED EMBODIMENTS

Coating of polished IC wafer surfaces by preferentially adsorbed surfactants or polymers can significantly eliminate scratching and redeposition of residue. The coating layer, however, should be weakly bonded to the wafer surfaces, and be readily swept away by abrasion during CMP process, so that the materials removal rate will not be significantly reduced. The coating layers should also be readily rinsed off by DI water, or alkaline solutions in the post-CMP cleaning processes. It has been discovered that the addition of a type of surfactant or a type of polymer into the CMP slurries can effectively serve the purposes outlined above providing the additive has a carbon chain length greater than about 16. A surfactant should have a hydrophobic end containing  $C_xH_{2x+1}$  with  $x > 16$ , or have ethylene oxide chains  $(OCH_2CH_2)_n$  with  $n > 8$ , or the mixture of both. The other end of the surfactant comprises functional hydrophilic moieties attached to the hydrophobic chain described above. These moieties have affinity to surface groups (i.e., silanol, siloxane, or hydroxylized metal films or lines) contained on wafer surfaces. These functional end groups are commonly polar moieties, such as, but not limited to, hydroxyl, ether, amine oxide, phosphine oxide, sulphoxide, carboxy, carbonyl, alkoxy, sulphonyl, sulphate and phosphonyl. The polymer may be a high molecular weight organic polymer containing a carbon backbone with functional moieties extending from the backbone. The functional moieties interact strongly with the wafer surface so as to provide a protective layer. The mechanism of interaction between the functional moieties and the hydroxyl surface is most likely, though not limited to, that observed in the hydrogen bonding of polar species (such as the interaction of hydroxyl groups). The polymer compound is further defined as a high molecular weight organic material, having a degree of polymerization of at least 5 (i.e., 5 repeating monomeric units), more preferably more than 10, and most preferably greater than 50. The carbon chain backbone of the polymer should have a carbon chain length of about 16 or greater. The polymer compound comprises a plurality of moieties having affinity to surface groups (i.e., silanol, siloxane, hydroxylized metal films or lines etc.) contained on wafer surfaces. These groups are commonly polar moieties, such as, but not limited to, hydroxyl, ether, amine oxide, phosphine oxide, sulphoxide, carboxy, carbonyl,

alkoxy, sulphonyl, sulphate and phosphonyl. The ratio of the number of the wafer surface affinity functional groups to the number of carbons in the backbone chain shall be between 1:1 to 1:200, preferably from 1:1 to 50, and most preferably from 1:1 to 1:10. It is also observed that block co-polymers of the above defined polymers have the same functions for the above mentioned applications. Examples of this type of molecule include, but not limited to, poly-vinyl alcohol, poly-vinylpyrrolidone, poly-methyl methacrylate, poly-formaldehyde, poly-ethylene oxide, poly-ethylene glycol, poly-methacrylic acid, polyacrylic acid and the mixture of the like.

10 The slurries of this invention may optionally comprise a dispersant. Aqueous CMP slurries contain submicron abrasive particles. The size of these particles is important to the performance of the slurry as well as to the resultant surface quality. If the abrasive particles agglomerate, the polishing removal rates may change and the surface quality may deteriorate. Dispersants can be included in the slurry formulation  
15 to prevent this agglomeration of abrasive particles. Dispersants can be anionic, cationic, or nonionic. The selection of the proper dispersant depends on many factors including the surface characteristics of the abrasive particles and the ionic nature of the slurry formulation. Some examples of ionic surfactants include sodium lauryl sulfate, cetyl-trimethyl ammonium bromide. Amino alcohols are also used as  
20 dispersants in slurries for CMP.

An oxidizing agent may also be present in the compositions of the present invention. Examples of common oxidizing agents are nitrates, iodates, chlorates, perchlorates, chlorites, sulphates, persulphates, peroxides, ozonated water, and  
25 oxygenated water. Oxidizing agents can be used in slurries for CMP at concentrations of about 0.01% to about 7% by weight. Generally they are used at concentrations of about 1% to about 7% by weight. An iodate is a preferred oxidizing agent.

Any metal oxide or other polishing abrasive (such as alumina, ceria, zirconia,  
30 silica, titania, barium carbonate, or diamond) may be used in the slurries of this invention.



One particularly useful polishing composition of this invention for the chemical mechanical polishing of semiconductor wafers having a metal and in particular a copper metal circuit is a polyacrylic acid composition that comprises an aqueous composition having a pH of under 5.0 and comprises

- 5 polyacrylic acid having a number average molecular weight of about 20,000 – 150,000, or blends of high and low number average molecular weight polyacrylic acids,
- up to 3.0% by weight of abrasive particles,
- 1-15% by weight of an oxidizer, preferably hydrogen peroxide,
- 10 50-5,000 ppm (parts per million by weight) of an inhibitor, and
- up to 3.0% by weight of a complexing agent, preferably, malic acid.

- A preferred polyacrylic acid polishing composition contains a blend of two or more polyacrylic polymers of a low molecular weight polyacrylic acid polymer
- 15 having a number average molecular weight of about 20,000-100,000 and a high number average molecular weight polymer of about 200,000 – 1,500,000. The weight ratio of low molecular weight polymer to high molecular weight polymer is about 10:1 to 1:10.

- 20 This polyacrylic acid polishing composition is an aqueous composition having a pH of under 5.0 and preferably about 2.8-4.2, and more preferably, 2.8-3.8. It has been found that a pH of 5.0 and above results in significant reduction in polishing of the copper in the semiconductor substrate

- 25 This polyacrylic acid composition contains about 0.05-1.0% by weight, based on the weight of the composition, of polyacrylic acid or a blend or mixture of polyacrylic acids at least one having a relatively high number average molecular weight and the other or others having a relatively low number average molecular weight.

30

The number average molecular weight of the polyacrylic acid is determined by GPC (gel permeation chromatography).

The polyacrylic acid used in the polyacrylic acid composition has a number average molecular weight of about 20,000 – 150,000, preferably 25,000 – 75,000 and more preferably 25,000 – 40,000. If a blend or mixture of two polyacrylic acids is used, a low number average molecular weight polymer having a molecular weight of about 20,000 – 100,000 and preferably 20,000 – 40,000 is used. The high number average polyacrylic acid has a molecular weight of about 200,000 – 1,500,000, preferably, 150,000 – 300,000. The weight ratio of the low molecular weight polyacrylic acid polymer to the high molecular weight polymer is about 10:1 to 1:10, preferably 4:1 to 1:4, and more preferably 2:1 to 1:2.

One particularly preferred blend comprises a polyacrylic polymer having a low number average molecular weight of about 30,000 and a polyacrylic polymer having a high number average molecular weight of about 250,000 in a 1:1 weight ratio.

It is possible to use additional low molecular weight polyacrylic acids in the blend such as polyacrylic acids having a number average molecular weight of 1,000 – 5,000.

It is possible to use very high molecular weight polyacrylic acid polymers (molecular weight over 1,500,000) or crosslinked polyacrylic acid polymers in these polishing compositions as an additional additive, by properly adjusting polishing conditions and other components of the composition. Also, it may be possible to use these high molecular weight or crosslinked polyacrylic acids in place of the aforementioned single polyacrylic acid or the blend of polyacrylic acids.

It is possible to use polymers of the acrylic group such as copolymers of acrylic acid, polymethacrylic acid, copolymers of methacrylic acid, polyacrylamides, acrylamide copolymers, polymethacrylamides, methacrylamide copolymers and a variety of other copolymers of the above and obtain an acceptable polishing composition.

Also, it is possible to form polyacrylic acid polymers that are biodegradable, photodegradable, or degradable by other means that can be used in this invention for the polishing composition. An example of such a composition is a biodegradable  
5 polyacrylic acid containing segments of poly(acrylate co methyl 2-cyanoacrylate).

The polyacrylic acid polishing composition can contain up to 3.0% by weight of abrasive particles described above. Preferably, the composition does not contain such particles.

10

The polyacrylic acid polishing composition contains about 1-15% by weight, preferably, 5-10% by weight, of an oxidizing agent such as hydrogen peroxide, iodates such as potassium iodate, nitrates such as cesium nitrate, barium nitrate, ammonium nitrate, mixtures of ammonium nitrate and cesium nitrate, carbonates such  
15 as ammonium carbonate, persulfates such as ammonium and sodium sulfate and perchlorates. Hydrogen peroxide is preferred in amounts of about 9% by weight.

The polyacrylic acid composition contains up to 3.0% and preferably, 0.1-1.0% of a complexing agent such as carboxylic acids containing two or more  
20 carboxylate groups with hydroxy groups as disclosed in Brancaloni et al US Patent 5,391,258 issued Feb. 21, 1995 which is hereby incorporated by reference. Typical complexing agents include straight chain mono- and dicarboxylic acids and their salts such as malic acid and malates, tartaric acid and tartarates, gluconic acid and gluconates, citric acid and citrates, malonic acid and malonates, formic acid and formates, lactic  
25 acid and lactates. Polyhydroxybenzoic acid and acid salts, phthalic acid and acid salts also can be used.

The polyacrylic acid composition also contains about 50-5,000 ppm (parts per million by weight) of an inhibitor such as BTA (benzotriazole) and TTA  
30 (tolyltriazole) or mixtures thereof that are preferred. Other inhibitors that can be used are 1-hydroxybenzotriazole, N-(1H-benzotriazole-1-ylmethyl)formamide, 3,5-dimethylpyrazole, indazole, 4-bromopyrazole, 3-amino-5-phenylpyrazole, 3-amino-4-

A Cruise K-12 Tensiometer was used to determine surface tension. For surface tension measurements, the density of the slurry is measured and recorded. Wafers, cut into square sections and cleaned via torch method, are measured to determine their thickness' and widths, and then placed in a clean area for future use.

5 The instrument is turned on and the balance is zeroed. Wafers, are attached to the balance via a clasp holder, and 80 ml of slurry is added to the appropriate sample container. During experimentation, the sample container will rise until the wafer is immersed in the slurry to a given depth. The data generated by the instrument is calculated based on weight differences experienced by the wafer as it penetrates the  
10 surface of the slurry. To determine surface tension, the surface tension software is opened, the plate method is selected, and sample parameters are entered. (e.g. Thickness, and width of the wafer, density of the slurry, and immersion depth.) The instrument is started and surface tension is calculated.

15 As seen in Table 1, the addition of PVP (Polyvinylpyrrolidone) into the slurry reduces the surface tension on both TEOS and BPSG wafer surfaces, indicating that the PVP adsorbed on the surface and formed a protection layer along the surfaces.

**Table 1:** Effect of additives on surface tension of wafers

Solution	Surface Tension on TEOS (Dyne/cm)	Surface Tension on BPSG (dyne/cm)
D. I. Water at 25C	54.3	68
Sample A without PVP	54.3	56
Sample B: Sample A + 0.2 wt% PVP	41.5	44

20

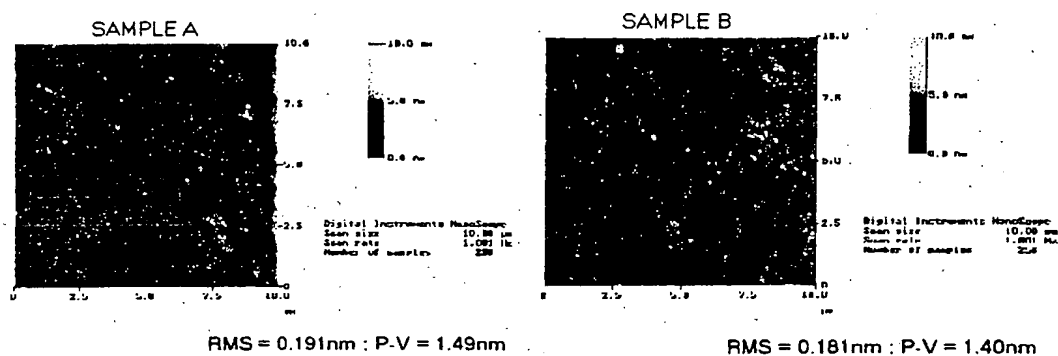
#### **Example 2:** Wafer surface roughness reduction

AFM images were taken of wafers from samples A & B. A Digital  
25 Instruments Dimension 5000 AFM was used to image the wafers. A 10 x 10 $\mu$ m scan size was chosen. RMS (root mean square) roughness was measured as well as P-V

(peak to valley) for all surface points. Center and edge points on the wafer were sampled.

5

Figure 1. AFM Images



As shown in figure 1, the addition of PVP improved the surface roughness significantly. Scratches were eliminated by addition of PVP.

10

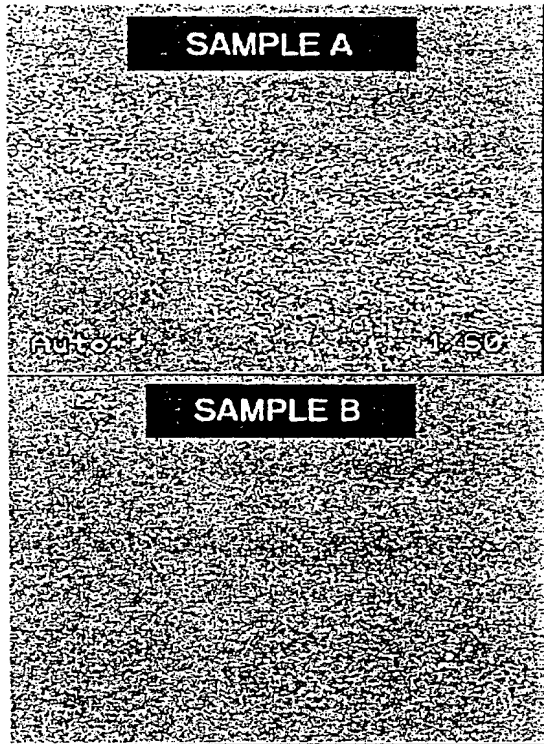
### Example 3: Prevention of slurry/residue re-deposition

To illustrate the effects of PVP on extreme surface roughening and slurry residue re-deposition, an underconditioned OXP-3000 was used in a slower table and platen speed process. Sample A without PVP was used as the polishing slurry under the given conditions. This was followed by Sample B with PVP. TEOS sheet wafers were polished, buffed with DI Water, cleaned with an ammonium hydroxide solution on an OnTrak DSS-200 scrubber, and reviewed under a Leica defect review optical microscope. The Leica was set at 5x objective, which translates to a 143x total screen magnification. Normarski prism mode was used to enhance contrast.

20

25

Figure 2. Leica Defect Review



As seen in Figure 2, slurry deposition or polishing debris re-deposition was eliminated by adding PVP into the polishing slurries, indicating that the PVP coating layer on the wafer prevented slurries or debris from directly depositing on wafer surface.

#### Example 4: Prevention of slurry/residue re-deposition

Several polymers and surfactants were used in this Example in which slurry/residue re-deposition was measured as in Example 3. It was surprisingly found that the polymers and surfactants which prevent the re-deposition of slurry/residue must have a carbon chain length of at least about 16. We cannot generally say that all

polymers and surfactants containing the functional moieties mentioned above will be effective. The molecules must be large enough to form a film thick enough to be a preventative to the slurry/residue re-deposition.

- 5 For the following slurry/redeposition tests, TEOS wafers were polished on a Strsbaugh 6DS-SP polisher under the following conditions. ILD1300 polishing slurry available from Rodel, Inc., Newark, DE was used with 0.2% by weight of the surfactant or polymer additive.

10

**Table 2.** Effect of carbon chain length.

Additive	Manufacturer	Type	Approximate Carbon Chain Length	Slurry/residue re-deposition/coating on wafer
Polyvinylpyrrolidone (Mw~10,000)	Sigma/Aldrich	Polymer	180	No
Polyvinylalcohol (Mw~40,000)	Air Products	Polymer	1600+	No
Amphoterge KJ-2	Lonza	Amphoteric Surfactant	9-15	Yes
BRIJ-58	ICI	Nonionic Surfactant	56	No
Zonyl FSP	Dupont	Anionic Surfactant	4-16	Yes

- 15 Table 2 shows that the carbon chain length must be about 16 or greater for the additive to be effective in preventing slurry/residue redeposition. It has also been found that suitable additives are particularly effective when used with a polishing pad with a relatively hard surface such as an OXP3000 pad available from Rodel, Inc., Newark, DE.

**Example 5 Polyacrylic acid polishing compositions**

5 An aqueous polishing Composition 1 was prepared by blending together the following constituents: 0.22 parts malic acid, 3000 ppm (part per million) benzo[triazole, 9.0 parts hydrogen peroxide with water to provide 100 parts of the composition and the pH was adjusted to 3.1. Then 0.09 parts polyacrylic acid having a number average molecular weight of 250,000 and 0.09 parts polyacrylic acid having a number average molecular weight of 30,000 were added.

10

A Mira polishing machine was used under the following conditions: 5 psi. down force, 100 rpm platen speed and 90 rpm head speed for 40 seconds; the second stage of polishing was 5 psi down force, 100 rpm platen speed, 25 rpm head speed for 40 seconds; and the third stage of polishing was 2 psi down force, 100 rpm platen speed and 90 rpm head speed for 220 seconds. The pad used was a Metals 26 pad made by Rodel Inc. and described in US Patent 6,022,268. The pad was pre-conditioned for 30 minutes with a 100 grit diamond disk (manufactured by Abrasives Technology, Inc.) and conditioned for 20 seconds between polishing of wafers.

20

The test wafers polished is a silicon wafer having a silicone dioxide layer with copper trenches or lines each having a width of 10  $\mu\text{m}$ , 25  $\mu\text{m}$  and 100  $\mu\text{m}$  and a thin copper layer is deposited on top of the wafer.

25

After polishing the dishing of each of the lines was measured at the center, middle and edge of the line and an average was determined. Because the polishing composition has high copper to barrier selectivity, the copper removal essentially stops when the barrier is reached. Therefore the dishing values reported in the following Table I include the barrier thickness. The results as shown below in Table I are considered acceptable.

30

An aqueous polishing Composition 2 was prepared which was identical to Composition 1 except the following mixture of polyacrylic acids was used: 0.09%



Polyacrylic Acid MW 1,250,00 + 0.09% Polyacrylic Acid MW 30,000. Polishing was carried out as above and the results are acceptable and shown in Table 1 below.

5 An aqueous polishing Composition 3 was prepared which was identical to Composition 1 except the following mixture of polyacrylic acids was used: 0.09% Polyacrylic Acid MW 750,000 + 0.09% Polyacrylic Acid MW 30,000. Polishing was carried out as above and the results are acceptable and shown in Table 1 below.

10 An aqueous polishing Composition 4 was prepared which was identical to Composition 1 except the following polyacrylic acid was used: 0.18% Polyacrylic Acid MW 30,000. Polishing was carried out as above and the results are acceptable and shown in Table 1 below.

15 An aqueous polishing Composition 5 was prepared identical to Composition 1 except all of the benzotriazole was replaced with tolyltriazole. Polishing was carried out under the following conditions: 5 psi. down force, 100 rpm platen speed and 90 rpm head speed for 60 seconds; the second stage of polishing was 5 psi down force, 100 rpm platen speed, 25 rpm head speed for 60 seconds; and the third stage of polishing was 2 psi down force, 100 rpm platen speed and 90 rpm head speed for 115  
20 seconds. The polishing results are acceptable and shown in Table 1 below.

TABLE 1

Composition 1

(0.09% 250,000 MW Polyacrylic Acid + 0.09% 30,000 MW Polyacrylic Acid)

5	10 um line	25 um line	100 um line
	Ave. 391	Ave. 493	Ave. 943

Composition 2

(0.09% 1,250,000 MW Polyacrylic Acid + 0.09% 30,000 MW Polyacrylic Acid)

10	10um line	25 um line	100 um line
	Ave. 316	Ave. 383	Ave. 637

Composition 3

(0.09% 750,000 MW Polyacrylic Acid + 0.09% 30,000 MW Polyacrylic Acid)

15	10um line	25 um line	100 um line
	Ave. 416	Ave. 441	Ave. 940

Composition 4

(0.18% 30,000 MW Polyacrylic Acid)

20	10um line	25 um line	100 um line
	Ave. 469	Ave. 715	Ave. 1007

Composition 5

(Identical to Composition 1 except tolyltriazole was substituted for benzotriazole)

25	10um line	25 um line	100 um line
	Ave. 354	Ave. 503	Ave. 757

**EXAMPLE 8 (COMPARATIVE EXAMPLE)**

- 30        The following polishing compositions containing polyacrylic acid illustrate compositions that do not provide adequate polishing results:

Composition 6

The composition is identical to Composition 1 except that 0.18% polyacrylic acid having a number average molecular weight of 1,800 was substituted for the polyacrylic acid blend used in Composition 1. Polishing was done in an identical manner as used with Composition 1 except the third stage of polishing was continued for 500 seconds. Polishing was inadequate since there was no removal of copper from the wafer.

10 Composition 7

The composition is identical to Composition 1 except that 0.18% polyacrylic acid having a number average molecular weight of 250,000 was substituted for the polyacrylic acid blend used in Composition 1. Polishing was done in an identical manner as used with Composition 1.

The results were as follows: 10um – 725, 25 um – 959, 100 um – 1581. The dishing value for the 100 um line is considered unacceptable.

20 Composition 8

The composition is identical to Composition 1 except that the pH was adjusted to 5.5. Polishing was done in an identical manner as used with Composition 1. Polishing was inadequate since there was no removal of copper from the wafer.

## CLAIMS

1. A composition useful for the polishing of integrated circuit surfaces  
comprising an organic polymer having a backbone comprised of at least 16  
5 carbon atoms, said polymer having a plurality of moieties with affinity to  
surface groups on said semiconductor wafer surface.
2. A composition according to claim 1 wherein said moieties consist of one  
or more of the following groups: hydroxyl, ether, amine oxide, phosphine  
10 oxide, sulphoxide, carboxy, carbonyl, alkoxy, sulphonyl, sulphate, and  
phosphonyl.
3. A composition according to claim 1 wherein said organic polymer is from  
the group consisting of poly-vinyl alcohol, poly-vinylpyrrolidone, poly-  
15 methyl methacrylate, poly-formaldehyde, poly-ethylene oxide, poly-  
ethylene glycol, and poly-methacrylic acid.
4. A composition useful for the polishing of integrated circuit surfaces  
comprising a surfactant having a carbon chain backbone comprised of at  
20 least 16 carbon atoms.
5. A method of polishing a semiconductor wafer substrate, wherein said  
substrate is pressed against a polishing pad, said substrate and said pad are  
moved relative to each other, and a polishing composition is applied to  
25 said pad during the polishing operation, said polishing composition  
comprising an organic polymer having a backbone comprised of at least 16  
carbon atoms, said polymer having a plurality of moieties with affinity to  
surface groups on said semiconductor wafer substrate.

6. An aqueous polishing composition for chemical mechanical polishing of semiconductor substrates having a pH under 5.0 that comprises polyacrylic acid having a number average molecular weight of about 20,000 – 150,000,  
5 up to about 3.0% by weight, based on the weight of the composition, of abrasive particles,  
1-15 % by weight, based on the weight of the composition, of an oxidizing agent,  
50-5000 parts per million by weight of an inhibitor, and  
10 up to 3.0% by weight, based on the weight of the composition, of a complexing agent.
7. The aqueous polishing composition of claim 6 having a pH of about 2.8 – 4.2 and in which the polyacrylic acid has a number average molecular  
15 weight of about 25,000 – 75,000 and is present in the composition in an amount of about 0.05 – 1.0% by weight, based on the weight of the composition.
8. An aqueous polishing composition for chemical mechanical polishing of semiconductor substrates having a pH under 5.0 that comprises  
20 a blend of at least two polyacrylic acids wherein one polyacrylic acid has a low number average molecular weight of about 20,000 – 100,000 and a second polyacrylic acid has a high number average molecular weight of about 200,000 – 1,500,000; wherein the weight ratio of the low number  
25 average molecular weight polyacrylic acid to the high number average molecular weight polyacrylic acid is about 10:1 to 1:10,  
up to about 3.0% by weight, based on the weight of the composition of abrasive particles,  
1-15 % by weight, based on the weight of the composition, of an oxidizing  
30 agent,  
50-5000 parts per million by weight of an inhibitor, and  
up to 3.0% by weight, based on the weight of the composition of a

complexing agent.

- 5 9. A method of polishing a semiconductor wafer substrate, wherein said substrate is pressed against a polishing pad, said substrate and said pad are moved relative to each other, and a polishing composition is applied to said pad during the polishing operation, said polishing composition comprising a surfactant having a carbon chain backbone comprised of at least 16 carbon atoms.
- 10 10. A method of polishing a surface of a semiconductor wafer comprising the steps of:
- (a) providing a polishing pad having a polishing surface;
  - (b) holding said wafer in a carrier such that the surface of the wafer is in contact with the polishing surface;
  - 15 (c) moving said carrier to provide both pressure on the surface of the wafer and relative lateral motion between the surface of the wafer and the polishing surface; and
  - (d) providing the aqueous polishing liquid of claim 6 or claim 8 at an interface between the surface of the wafer and the polishing surface.
- 20

**AMENDED CLAIMS**

[received by the International Bureau on 31 January 2001 (31.01.01);  
original claims 1-10 replaced by new claims 1-7 (3 pages)]

1. An aqueous polishing composition for chemical mechanical polishing  
5 of semiconductor substrates having a pH under 5.0 that comprises  
a blend of at least two polyacrylic acids, wherein one polyacrylic acid has  
a low number average molecular weight of about 20,000 – 100,000 and a  
second polyacrylic acid has a high number average molecular weight of  
10 about 200,000 – 1,500,000; wherein the weight ratio of the low number  
average molecular weight polyacrylic acid to the high number average  
molecular weight polyacrylic acid is about 10:1 to 1:10,  
up to about 3.0% by weight, based on the weight of the composition of  
abrasive particles,  
1-15 % by weight, based on the weight of the composition, of an oxidizing  
15 agent,  
50-5000 parts per million by weight of an inhibitor, and  
up to 3.0% by weight, based on the weight of the composition of a  
complexing agent.

20 2. The aqueous polishing composition of claim 1 in which the blend  
consists of two polyacrylic acids, wherein one polyacrylic acid has a low  
number average molecular weight of about 20,000 – 40,000 and a second  
polyacrylic acid has a high number average molecular weight of about  
200,000 – 300,000; wherein the weight ratio of the low number average  
25 molecular weight polyacrylic acid to the high number average molecular  
weight polyacrylic acid is about 4:1 to 1:4

3. The aqueous polishing composition of claim 1 in which the oxidizing  
agent consists of hydrogen peroxide.

4. The aqueous polishing composition of claim 1 in which the inhibitor is from the group of benzotriazole, tolyltriazole or mixtures thereof.

5. The aqueous polishing composition of claim 1 in which the  
5       complexing agent is a carboxylic acid having at least two carboxyl groups and a hydroxyl group.

6. The aqueous polishing composition of claim 1 having a pH of 2.8 to 4.2 in which the blend consists of two polyacrylic acids, wherein one  
10       polyacrylic acid has a low number average molecular weight of about 20,000 -- 40,000 and a second polyacrylic acid has a high number average molecular weight of about 200,000 -- 300,000; wherein the weight ratio of the low number average molecular weight polyacrylic acid to the high  
15       number average molecular weight polyacrylic acid is about 4:1 to 1:4, the oxidizing agent consists of hydrogen peroxide, the inhibitor is from the group of benzotriazole, tolyltriazole or any mixtures thereof and the  
      complexing agent is a carboxylic acid having two carboxyl groups and a hydroxyl group.



7. A method of polishing a surface of a semiconductor wafer comprising the steps of:

(a) providing a polishing pad having a polishing surface;

5 (b) holding said wafer in a carrier such that the surface of the wafer is in contact with the polishing surface;

(c) moving said carrier to provide both pressure on the surface of the wafer and relative lateral motion between the surface of the wafer and the polishing surface; and

10 (d) providing the aqueous polishing composition of claim 1 at an interface between the surface of the wafer and the polishing surface.

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 C09K3/14 H01L21/302 C09G1/02

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C09K H01L C09G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

CHEM ABS Data, EPO-Internal, WPI Data, PAJ, COMPENDEX, INSPEC

### C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 352 277 A (SASAKI SHIGEO) 4 October 1994 (1994-10-04) claim 1 ---	1-5,9
X	US 5 704 987 A (GILHOOLY JAMES ALBERT ET AL) 6 January 1998 (1998-01-06) column 3, line 3 - line 36 ---	1-5,9
X	US 5 860 848 A (LONCKI SCOTT B ET AL) 19 January 1999 (1999-01-19) claims 1,7-10 ---	1-5,9
X	US 4 752 628 A (PAYNE CHARLES C) 21 June 1988 (1988-06-21) claim 1 ---	1-5,9
Y		6-8,10
	--- -/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

\*A\* document defining the general state of the art which is not considered to be of particular relevance

\*E\* earlier document but published on or after the international filing date

\*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

\*O" document referring to an oral disclosure, use, exhibition or other means

\*P\* document published prior to the international filing date but later than the priority date claimed

\*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

\*& document member of the same patent family

Date of the actual completion of the international search

11 December 2000

Date of mailing of the international search report

22 12. 2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Shade, M

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 0 913 442 A (HITACHI LTD) 6 May 1999 (1999-05-06) embodiments 4 and 5 -----	6-8, 10

**Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)**

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.:  
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:  
see FURTHER INFORMATION sheet PCT/ISA/210
3. ☐ Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

**Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)**

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

**Remark on Protest**

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

## Continuation of Box I.2

Present claims 1 to 4 relate to an extremely large number of possible compositions of polymers or surfactants and present claims 5 and 9 relate to an extremely large number of possible methods of polishing. Support within the meaning of Article 6 PCT and disclosure within the meaning of Article 5 PCT is to be found, however, for only a very small proportion of the compositions and methods claimed. In the present case, the claims so lack support, and the application so lacks disclosure, that a meaningful search over the whole of the claimed scope is impossible. Consequently, the search has been carried out for those parts of claims 1 to 5 and 9 which appear to be supported and disclosed, namely those parts relating to the compositions and methods of examples 1 to 4.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 5352277	A	04-10-1994	JP 2158684 A	19-06-1990
			JP 2714411 B	16-02-1998
			DE 68921570 D	13-04-1995
			DE 68921570 T	12-10-1995
			EP 0373501 A	20-06-1990
			KR 151844 B	01-10-1998
US 5704987	A	06-01-1998	NONE	
US 5860848	A	19-01-1999	AU 5952096 A	18-12-1996
			EP 0840664 A	13-05-1998
			WO 9638262 A	05-12-1996
US 4752628	A	21-06-1988	DE 3815578 A	24-11-1988
			JP 63318257 A	27-12-1988
EP 0913442	A	06-05-1999	JP 11135466 A	21-05-1999
			CN 1216727 A	19-05-1999
			US 6117775 A	12-09-2000

pyrazolecarbonitrile, 1-methylimidazole, Indolin QTS and the like.

The polyacrylic acid composition may contain pH buffers such as amines, and may contain surfactants, deflocculants, viscosity modifiers, wetting agents, cleaning  
5 agents and the like.

The following are typical polishing pads that can be used with the novel polishing composition and with the polyacrylic acid composition of this invention to polish semiconductors: metals pad described in Roberts et al US Patent 6,022,268  
10 issued Feb. 8, 2000, pads containing polishing particles described in Cook et al US Patent 6,022,264 issued Feb. 8, 2000, pads described in Cook et al US Patent 5,489,233 issued Feb. 6, 1996, polymer impregnated fiber matrices typified by pads sold by Rodel, Inc. under the trade name SUBA, pads of a polymer sheet containing void spaces effected by in situ production or incorporation of hollow filler materials  
15 (typically pads sold by Rodel, Inc. under the trade names POLITEX AND IC1010), pads of polymer sheets containing solid particles added as fillers, which may optionally contain void spaces, effected either by in situ production or by incorporation of hollow filler materials (typically pads sold by Rodel Inc. under the trade names MH), and composite pads consisting of multiple layers of materials  
20 whose outer substrate contacting surface consists of a pad selected from one of the above.

In the examples presented below, we demonstrate the reduction of wafer surface tension resulting from the adsorption of the above mentioned additives in the  
25 slurries. Examples of the surface roughness improvement and prevention of slurry/residue redeposit are also given. All parts and percentages are on a weight basis and molecular weights are determined by gel permeation chromatography unless otherwise indicated.

30

**Example 1:** Wafer surface tension reduction by additives in slurries

**THIS PAGE BLANK (USPTO)**